

# Comparative Study of Scattering and Osmotic Properties of Synthetic and Biopolymer Gels

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The physiological functions of biological macromolecules strongly depend upon their conformation. Study of the thermodynamic and structural aspects of ion/polymer interactions has the potential to contribute to a more comprehensive understanding of ion mediated structural organization of charged biomacromolecules (e.g., nucleic acids, proteins, proteoglycans, etc.) within cells or extracellular matrix.

Interactions between  $\text{Ca}^{2+}$  ions and charged biomacromolecules are ubiquitous in biology. They are implicated in a wide-range of physiological processes including nerve excitation, muscle contraction, ion channel dynamics, etc. However, the mechanism of calcium association and interaction with charged polymers is poorly understood from a polymer physics perspective. We are performing fundamental experimental and simulation studies on polyelectrolyte solutions and hydrogels in order to understand the mechanisms of interactions of  $\text{Ca}^{2+}$  ions with biopolymers, specifically on their structure and thermodynamic properties. Hydrogels are particularly well-suited model systems to study ion-polymer interactions. While in solutions of charged macromolecules changes in electrostatic interactions (e.g., caused by addition of multivalent ions) may lead to phase separation, in gels macroscopic phase separation does not occur.

Previously [1-3] we investigated physicochemical interactions occurring among charged polymer gels [e.g., DNA, sodium polyacrylate (PAA)] and certain divalent cations ( $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , etc.) under nearly physiological conditions. The experiments show that small increases in the concentration of multivalent cations cause these anionic polyelectrolyte gels to collapse. This phenomenon was determined to be a reversible process by decreasing the  $\text{Ca}^{2+}$  concentration in the solution surrounding the swollen network. We also found that the elastic modulus is practically independent of the  $\text{CaCl}_2$  concentration, i.e.,  $\text{Ca}^{2+}$  ions do not form permanent bridges between neighboring polymer chains. The reversible nature of the volume transition and the absence of measurable effect of calcium on the elastic modulus indicate that calcium binding is not permanent. In the present work, we investigate the effect of  $\text{Ca}^{2+}$  ions on the osmotic and scattering properties of polyelectrolyte gels.

Figure 1 shows the neutron scattering intensity  $I(q)$  as a function of the scattering vector  $q$  for PAA and DNA gels. The main features of the scattering spectra of these gels are identical. At low  $q$  a power law behavior is observed caused by scattering from surfaces. At intermediate  $q$  the scattering intensity varies as  $q^{-1}$ .

This behavior is typical of scattering from rod-like structures. At high  $q$  the scattering response can be described by the Ornstein-Zernike expression [4]. The striking similarity between the SANS spectra of DNA and PAA gels indicates that the thermodynamic interactions that govern the organization of these two entirely different molecules are practically independent of the chemical details (e.g., sequence of the DNA base pairs).

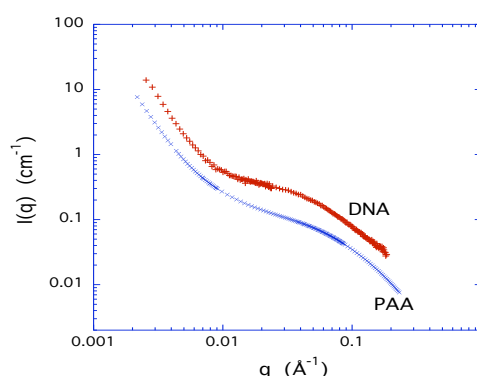


Figure 1. SANS spectra of PAA and DNA gels in 40 mM NaCl solution containing 0.1 mM  $\text{CaCl}_2$ .

The intensity of the neutron scattering signal is related to the osmotic pressure, since the scattering intensity is governed by the osmotic compressibility of the system. We will demonstrate that combination of scattering and osmotic measurements allows us to determine the characteristic size of the structural elements that contribute to the osmotic concentration fluctuations, and yields important information on the effect of ions on the structure and thermodynamic properties at both molecular and supermolecular level.

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